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Toxicity of Pyrethroids to Marine Invertebrates and Fish
A Literature Review and Test Results with Sediment-Sorbed Chemicals

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16. ABSTRACT

Data on acute and chronic toxicity of permethrin, fenvalerate, cypermethrin, and flucythinate to marine invertebrates and fishes are reviewed. Laboratory toxicity tests were conducted with sediment-source fenvalerate and cypermethrin under static and flow-through conditions to determine the degree of contamination necessary to achieve acute, lethal effects on mysids (Mysidopsis bahia), grass shrimp (Palaemonetes pugio), and pink shrimp (Penaeus duorarum). Mortality was observed among test animals only in systems where concentrations of sediment-source pyrethroids were sufficient to establish lethal concentrations in overlying water through sediment-water partitioning. For fenvalerate, lethal effects occurred at sediment concentrations of 0.1 mg/kg (static and flow-through) for mysids and grass shrimp and 10 mg/kg for pink shrimp. Sediment concentrations of cypermethrin [0.1 mg/kg (static) or 1.0 mg/kg (flowthrough)] resulted in mortality among mysids and grass shrimp, whereas 1.0 mg/kg was the only test concentration that caused mortality among pink shrimp in static or flow-through tests systems. Correspondence between aqueous concentrations and LC50s for test animals demonstrate the importance of quantitating the bioavailable portion of pyrethroids in field samples to characterize accurately environmental risk associated with pyrethroid runoff after agricultural applications.

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TOXICITY OF PYRETHROIDS TO MARINE INVERTEBRATES AND FISH: A LITERATURE REVIEW AND TEST RESULTS WITH SEDIMENT-SORBED CHEMICALS

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Abstract—Data on the acute and chronic toxicities of permethrin, fenvalerate, cypermethrin and flucythrinate to marine invertebrates and fish are reviewed. Generally, crustaceans are more sensitive than fish; oysters are comparatively insensitive. The mysid *Mysidopsis bahia* consistently is among the most sensitive crustaceans tested, with 96-h LC50s of less than 0.02 μg/L for permethrin and of less than 0.01 μg/L for fenvalerate, cypermethrin and flucythrinate. The potential for chronic toxicity to fish is minimal for permethrin, moderate for fenvalerate and relatively great for flucythrinate.

Laboratory toxicity tests were conducted with sediment-source fenvalerate and cypermethrin under static and flow-through conditions to determine the degree of contamination necessary to achieve acute lethal effects on mysids, grass shrimp (*Palaemonetes pugio*) and pink shrimp (*Penaeus duorarum*). Mortality was observed in test animals only in systems where the concentrations of sediment-source pyrethroids were sufficient to establish lethal concentrations in the overlying water through sediment/water partitioning. For fenvalerate, lethal effects occurred at nominal sediment concentrations of 0.1 mg/kg (static and flow-through) for mysids and grass shrimp and at 10 mg/kg for pink shrimp. Nominal sediment concentrations of cypermethrin of 0.1 mg/kg (static) or 1.0 mg/kg (flow-through) resulted in mortality in mysids and grass shrimp, whereas 1.0 mg/kg was the only test concentration that caused mortality in pink shrimp in the static and flow-through test systems. The correspondence between aqueous concentrations and LC50s for test animals demonstrated the importance of quantitating the bioavailable portion of pyrethroids in field samples to characterize accurately the environmental risk associated with pyrethroid runoff after agricultural applications.

Keywords—Pyrethroids Insecticides Toxicity Marine organisms Sediment-sorbed chemicals

INTRODUCTION

Estuarine animals may be exposed to pyrethroids after applications to agricultural crops (e.g., corn, cotton, rice, vegetables) in coastal areas or by discharges from pyrethroid manufacturing, formulating or distribution centers. Pyrethroids are acutely toxic to estuarine animals in laboratory tests at concentrations of 0.01 μg/L or less [1], warranting their classification as "supertoxic" chemicals [2]. Also, pyrethroids generally have octanol/water partition coefficients of 10,000 or greater [1,3], indicating significant potential for bioaccumulation by aquatic organisms. However, because pyrethroids readily sorb and bind to organic and inorganic particulate matter [4-7], it is difficult to predict the toxic effects on aquatic biota after pyrethroid runoff from agricultural areas or discharges into particulate-laden habitats. Thus, the predictions of effects often are disputed.

In this article we (a) review the published data on the toxicity and bioaccumulation of several pyrethroids to marine fish and invertebrates, (b) present results of laboratory toxicity tests conducted with sediment-sorbed fenvalerate and cypermethrin in static and flow-through saltwater test systems

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and (c) discuss criteria for comparing laboratory toxicity test results with exposure-response data from marine systems that receive pyrethroids.

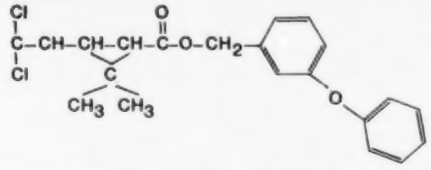
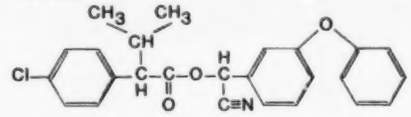
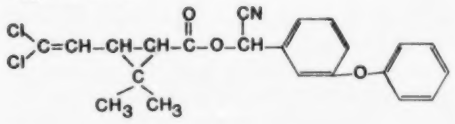
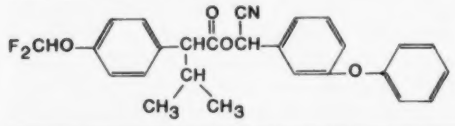
LITERATURE REVIEW

We reviewed the toxicity data on permethrin, fenvalerate, cypermethrin and flucythrinate for marine invertebrates and fish. Only scattered, incidental toxicity data were available on other pyrethroid insecticides, and few, if any, marine species were included. The four pyrethroids reviewed here are soluble in seawater at concentrations of 50 μg/L or less, have octanol/water partition coefficients, expressed as log *P* values, of 5.9 or greater and are registered for a variety of agricultural uses (Table 1). Permethrin was among the first pyrethroid insecticides to be made available commercially and it has one of the largest markets. It is approved for use on a variety of major crops (grains, cereals, cotton) and in specialty markets (various vegetables, fruits and ornamentals) [8]. A considerable amount of marine toxicity data is available for fenvalerate, partly because of its wide use (grains, cereals, vegetables, fruits, cotton) [8] and partly because of its selection as a test chemical for a comparative toxicity testing program at our laboratory [9,10]. Fewer data were available for cypermethrin and flucythrinate, which were more recently put on the market.

Permethrin

Mysids (*Mysidopsis bahia*) and stone crabs (*Menippe mercenaria*) were the most sensitive

Table 1. Selected physical and chemical properties and agricultural uses of permethrin, fenvalerate, cypermethrin and flucythrinate

Chemical and structure	Properties		Agricultural uses[a]
Permethrin 	Mol. wt.[a] Solubility[b] log P[c]	391.3 50 6.5	Corn Cotton Fruits Soybeans Vegetables
Fenvalerate 	Mol. wt.[a] Solubility[b] log P[c]	419.9 24 6.2	Corn Cotton Fruits Soybeans Vegetables
Cypermethrin 	Mol. wt.[d] Solubility[e] log P[f]	416.3 5–10 5.9	Cotton Fruits Vegetables
Flucythrinate 	Mol. wt.[d] Solubility[b] log P[c]	451.5 49 6.2	Cotton Fruits Vegetables

[a]From ref. 8.
[b]μg/L seawater [3].
[c]Log (concentration of pyrethroid in octanol/concentration of pyrethroid in water) [3].
[d]From ref. 23.
[e]For fresh water [24].
[f]From ref. 14.

invertebrates tested (Table 2); 96-h LC50s were 0.02 μg/L [3,11]. For other crustaceans, 96-h LC50s ranged from 0.13 to 2.2 μg/L. Borthwick and Walsh [11] reported a 48-h EC50 for oyster larvae (*Crassostrea virginica*) of greater than 1,000 μg/L. Of the five 96-h LC50s reviewed for marine fish, that for Atlantic silversides (*Menidia menidia*) was lowest at 2.2 μg/L [3]. The values for the other four species ranged from 4.0 to 12.0 μg/L. A 28-d early life stage (ELS) test with sheepshead minnow (*Cyprinodon variegatus*) produced a no observed effect concentration (NOEC) of 10 μg/L [12], a value comparable with the 96-h LC50 of 7.8 μg/L reported by Schimmel et al. [3]. Hansen et al. [12] reported a mean bioconcentration factor (BCF) of 480 for sheepshead minnow; a BCF of 1,900 was reported for oysters by Schimmel et al. [3].

Fenvalerate

Larval grass shrimp (*Palaemonetes pugio*) were the most sensitive marine invertebrate tested (Table 3); a 96-h LC50 of less than 0.003 μg/L was calculated from the data of McKenney and Hamaker [13]. For five other species of marine crustaceans, the 96-h LC50s ranged over two orders of magnitude, from 0.008 μg/L for mysids to 0.84 μg/L for pink shrimp (*Penaeus duorarum*) [3]. For oyster larvae, the 48-h EC50 was greater than 1,000 μg/L [11]. The 96-h LC50 was 1,600 μg/L for amphioxus (*Branchiostoma coribaeum*) [14]. The 96-h LC50s for fenvalerate ranged from 0.3 to 5.4 μg/L for nine species of marine fish. The results of 28- to 42-d ELS tests with five species of marine fish produced NOEC values that ranged from 0.060 μg/L for California grunion (*Leuresthes tenuis*) to 1.2 μg/L for Gulf toadfish (*Opsanus beta*) [10]. These data suggest that chronic effects may be induced in some fish species at concentrations as low as 0.2 of the acute LC50. BCF values of 570 for sheepshead minnows [12] and 4,700 for oysters [3] have been reported.

Table 2. Toxicity of permethrin to marine invertebrates and fish

	96-h LC50 (μg/L)	Reference
Acute toxicity to invertebrates		
Menippe mercenaria	0.02[a]	[11]
Mysidopsis bahia	0.02	[3]
Crangon septemspinosa	0.13[a]	[15]
Nitocra spinipes	0.15[a]	[25]
Penaeus duorarum	0.22	[3]
Penaeus aztecus	0.34[a]	[1]
Homarus americanus	0.73[a]	[15]
Uca pugilator	2.2[a]	[1]
Crassostrea virginica	>1,000[b]	[11]
Acute toxicity to fish		
Menidia menidia	2.2	[3]
Mugil cephalus	5.5	[3]
Alburnus alburnus	4 to 8[a]	[25]
Cyprinodon variegatus	7.8	[3]
Salmo salar	12.0[a]	[15]
Chronic toxicity (28-day ELS NOEC)		
Cyprinodon variegatus	10	[12]
Bioconcentration (BCF)		
Cyprinodon variegatus	480	[12]
Crassostrea virginica	1,900	[3]

ELS NOEC, early life stage no observed effect concentration.
[a]LC50 from static toxicity test.
[b]EC50 from 48-h static toxicity test based on larval development.

Table 3. Toxicity of fenvalerate to marine invertebrates and fish

	96-h LC50 (μg/L)	Reference
Acute toxicity to invertebrates		
Palaemonetes pugio	<0.003	[13]
Mysidopsis bahia	0.008	[3]
Crangon septemspinosa	0.04[a]	[15]
Homarus americanus	0.14[a]	[15]
Nitocra spinipes	0.38[a]	[25]
Penaeus duorarum	0.84	[3]
Crassostrea virginica	>1,000[b]	[11]
Branchiostoma caribaeum	1,600	[14]
Acute toxicity to fish		
Menidia menidia	0.3	[3]
Leuresthes tenuis	0.3	[9]
Alburnus alburnus	0.3[a]	[25]
Mugil cephalus	0.6	[3]
Menidia peninsulae	1.0	[9]
Menidia beryllina	1.0	[9]
Salmo salar	1.2[a]	[15]
Opsanus beta	2.4	[9]
Opsanus beta	5.4	[3]
Cyprinodon variegatus	5.0	[3]
Chronic toxicity (28-d ELS NOEC)		
Leuresthes tenuis	0.060	[10]
Menidia menidia	0.062	[10]
Menidia peninsulae	0.083	[10]
Cyprinodon variegatus	0.56	[12]
Opsanus beta	1.2	[10]
Bioconcentration (BCF)		
Cyprinodon variegatus	570	[12]
Crassostrea virginica	4,700	[3]

ELS NOEC, early life stage no observed effect concentration.
[a]LC50 from static toxicity test.
[b]EC50 from 48-h static toxicity test based on larval development.

Cypermethrin

Hill [1] reported a 96-h LC50 of 0.005 μg/L for mysids. However, at our laboratory, we obtained a 96-h LC50 of 0.056 μg/L for the same species. The 96-h LC50s (Table 4) for five other marine crustaceans ranged from 0.016 μg/L for grass shrimp [14] to 0.20 μg/L for fiddler crabs (*Uca pugilator*) [1]. Two species of oysters were tested [1]: a 96-h EC50 of 370 μg/L was based on shell deposition by *C. virginica* and a 48-h EC50 of greater than 2,300 μg/L for *C. gigas* was based on larval development. Only two 96-h LC50s were reported for cypermethrin in marine fish: 1.0 μg/L for sheepshead minnow [1] and 2.0 μg/L for Atlantic salmon (*Salmo salar*) [15]. No chronic toxicity data or bioaccumulation information were found in the literature for cypermethrin and marine species.

Flucythrinate

Flucythrinate was tested at our laboratory by Schimmel et al. [3]. The LC50s for mysids, pink shrimp and sheepshead minnows were 0.008, 0.22 and 1.1 μg/L, respectively (Table 4). A 28-d NOEC for sheepshead minnows of 0.032 μg/L [12] indicates the potential for chronic effects on a marine fish at concentrations as low as 0.03 of the acute effect concentrations. No other toxicity data were found for marine species. Hansen et al. [12] reported an estimated BCF of less than 1,800 for sheepshead minnows (no detectable flucythrinate in fish after 28 d of exposure to 0.27 μg/L).

Table 4. Toxicity of cypermethrin and flucythrinate to marine invertebrates and fish

	96-h LC50 (μg/L)	Reference
Cypermethrin		
Acute toxicity to invertebrates		
Mysidopsis bahia	0.005	[1]
Mysidopsis bahia	0.056	ERL/GB unpublished data
Palaemonetes pugio	0.016	[14]
Penaeus duorarum	0.036	[1]
Homarus americanus	0.040[a]	[15]
Crangon septemspinosa	0.010[a]	[15]
Uca pugilator	0.20	[1]
Crassostrea virginica	370[b]	[1]
Crassostrea gigas	>2,300[c]	[1]
Acute toxicity to fish		
Cyprinodon variegatus	1.0	[1]
Salmo salar	2.0[a]	[15]
Flucythrinate		
Acute toxicity to invertebrates		
Mysidopsis bahia	0.008	[3]
Penaeus duorarum	0.22	[3]
Acute toxicity to fish		
Cyprinodon variegatus	1.1	[3]
Chronic toxicity (28-d ELS NOEC)		
Cyprinodon variegatus	0.032	[12]

ELS NOEC, early life stage no observed effect concentration.
[a]LC50 from static toxicity test.
[b]EC50 from 96-h toxicity test based on shell deposition.
[c]EC50 from 48-h toxicity test based on larval development.

SUMMARY OF TOXICITY DATA

Pyrethroids are extremely toxic to marine crustaceans in laboratory tests. Fish generally are less sensitive than crustaceans; oysters are relatively insensitive. The potential for chronic toxicity to marine fish at exposure concentrations that are less than acutely toxic is minimal for permethrin, moderate for fenvalerate and relatively great for flucythrinate. However, because pyrethroids tend to sorb to particulate matter [1], chronic exposures may not occur other than under laboratory test conditions. Like organochlorine insecticides, pyrethroids have relatively large octanol/water partition coefficients [1,13]. Unlike organochlorines, however, most pyrethroids are readily metabolized by fish [16], which results in relatively low BCFs. The BCFs for oysters are an order of magnitude greater than those for fish, apparently because of slower rates of metabolism or depuration of pyrethroids by oysters or exposures through feeding and aqueous uptake. Sorption, biodegradation and metabolism of pyrethroids may render these insecticides less toxic in natural systems than standard laboratory test data would indicate.

TOXICITY OF SEDIMENT-SORBED PYRETHROIDS

To determine the extent to which sediment-sorbed pyrethroids are toxic to marine crustaceans, we tested fenvalerate and cypermethrin in laboratory systems. Based on the results of pilot studies, the nominal sediment fenvalerate concentrations of 0.1, 1.0 and 10 mg/kg were tested; cypermethrin was tested at sediment concentrations of 0.01, 0.1 and 1.0 mg/kg.

METHODS

Test sediments

Organic sediment was dredged from Santa Rosa Sound, Florida, near the Gulf Breeze laboratory, sun-dried, sterilized (dry heat) at 120°C for 2 h, pulverized and sieved to 1 mm in preparation

for testing. The sediment was 80% sand and 20% silt and contained 6% organic matter, as determined by weight loss upon ignition [17]. Two kilograms of prepared organic sediment was mixed with 200 ml of acetone that contained a measured amount of fenvalerate or cypermethrin until it was dry and granular. This contaminated sediment was combined with 25 kg of washed, quartz beach sand in a 120-liter stainless steel drum and mixed on a drum roller at 10 rpm for 2 h to produce homogeneous sediment at the desired test concentration. Control sediments were prepared in a similar manner, except that no insecticide was added to the acetone. The test sediments were approximately 95% sand and 5% silt and contained 0.6% organic matter. Tests with fenvalerate were conducted in May and June 1985; cypermethrin was tested in June and July 1985.

Two 60-liter aquaria (100 cm × 30 cm × 20 cm) received equal amounts (14.5 kg) of sediment for each test concentration. The sediment was spread to a uniform 3-cm depth throughout the aquaria. Two 3.8-liter jars fitted with two screened (140-μm nylon mesh) openings, 3 cm in diameter and placed 1 cm from the bottom, were added to each aquarium to hold grass shrimp during testing. For mysids, each aquarium contained two or four incubation cups, which were 13.7-cm-diameter glass culture dishes with a 25-cm-high collar of 363-μm nylon mesh. Each jar and incubation cup was placed on the glass bottom of an aquarium and test sediment was added to a depth of 3 cm (equal to the depth of sediment surrounding the container). A separate batch of sediment was made for tests on pink shrimp and distributed into aquaria without jars or incubation cups.

When sediment had been added to all aquaria, filtered (20-μm) seawater was added to each to a depth of 3 cm above the sediment surface. After a 90-min wetting period, the aquaria were filled with seawater (50 liters) and left for 48 h with gentle aeration to allow all surfaces to sorb pyrethroid. Sediment samples were then collected for time 0 analyses; then animals added and the static test begun. After 10 d, filtered seawater was added to each aquarium at the rate of 23 L/h for 48 h. Another batch of test animals was then added to each aquarium and a flow-through test begun.

Test animals

Adult grass shrimp (*Palaemonetes pugio*) were collected from shoreline habitats in Santa Rosa Sound. Mysids (*Mysidopsis bahia*), 5 to 7 d old at test initiation, were from our laboratory cultures. Adult pink shrimp (*Penaeus duorarum*) were purchased from a local bait dealer and maintained in the laboratory for two weeks before testing. Grass shrimp and mysids were added to their respective containers (10 grass shrimp per jar; either 8 or 10 mysids per incubation cup, depending on availability of mysids). Ten pink shrimp were added to separate aquaria, except for the cypermethrin flow-through test in which 20 shrimp were tested per aquarium. Grass shrimp and pink shrimp were observed each day; any dead animals were removed. All grass shrimp were removed from the systems on day 4; pink shrimp were observed for 10 d. Because the mysid containers had to be removed from test systems in order to count the number of survivors and this could not be accomplished without disrupting the sediment, half of the mysid containers were removed, without replacement, on day 4 and the mysids in the remaining containers were counted on day 10.

Test conditions

All tests were conducted in a room-temperature waterbath (25 ± 2°C). The salinity of the filtered seawater ranged from 22 to 28‰ for fenvalerate tests and from 25 to 31‰ for cypermethrin tests. Temperature and salinity were monitored continuously. Dissolved oxygen was measured at least twice each week; values ranged from 6.0 to 8.0 mg/L during all tests. Suspended solids were quantitated three times during each 10-d test, and total organic carbon (TOC) four times. A 200-ml water sample was passed through a tared, 0.45-μm Nuclepore filter, dried to constant weight at 103°C and weighed to determine suspended solids [17]. For all tests, suspended solids averaged 1.8 mg/L (SD 1.75, $n = 74$); the means for each sample date ranged from 0.38 to 3.0 mg/L. The data from static and flow-through tests were similar. A 5-ml water sample was frozen (−10°C) for up to 6 months before TOC analyses were conducted on a Beckman IR TOC analyzer [17]. The mean TOC concentration for fenvalerate tests was 56.8 μg C/L (SD 9.31, $n = 57$); for cypermethrin, TOC averaged 12.0 μg C/L (SD 12.6, $n = 67$). During fenvalerate tests, the daily means ranged from 43.0 to 58.9 μg/L; for cypermethrin tests, the daily means ranged from 8.0 to 37.9 μg/L. The differences between tests may reflect seasonal changes in TOC concentrations in seawater. Tests were conducted under a 12-h light:12-h dark photoperiod that incorporated 2 h of reduced light intensity (dusk and dawn) during the first and last 2 h of the light period.

Pyrethroid analyses

Water and sediment samples were collected from the test systems, outside of the animal containers, on days 0, 4 and 10, and water additionally on day 6 for both static and flow-through tests with fenvalerate and cypermethrin. One liter of water was extracted twice with 100 ml petroleum ether, the solvent dried, collected in a Kuderna-Danish evaporator and concentrated to approximately 1 ml following procedures described by Lores et al. [18]. Sediment samples, 10 g wet weight, were air-dried overnight. Dried sediment was added to a Chromoflex column (9 mm i.d.) and wetted with 2 to 3 ml distilled water. Pyrethroids were eluted from sediment with 40 ml 1:1 acetone:acetonitrile (v/v) into a bottle containing 30 ml 2% Na_2SO_4 (aqueous, w/v). The eluate was extracted twice with 20 ml petroleum ether and the extract processed as described for water sample extracts. Sample extracts were quantitated on a Hewlett-Packard No. 5730 gas chromatograph equipped with electron-capture detectors (300°C) and a 2-m 5% OV 210 column maintained at 250°C (same as for the injection port). These methods provided a detection limit of 0.02 μg/L for pyrethroids in water and of 0.005 mg/kg in sediment.

RESULTS

Fenvalerate

Fenvalerate concentrations measured in sediment during the static and flow-through experiments generally were near the desired nominal values, providing order-of-magnitude differences between test concentrations (Table 5). During the 1-month period of the consecutive static and flow-through tests, the concentrations of fenvalerate measured in sediments ranged from 8.4 to 13 mg/kg at the high test concentration, from 0.95 to 1.8 mg/kg at the intermediate concentration and from 0.097 to 0.19 mg/kg at the low concentration. Fenvalerate measured in the water in static test systems ranged from 0.2 to 1.9 μg/L, from 0.06 to 0.17 μg/L and from undetectable (<0.02 μg/L) to 0.03 μg/L at the high, intermediate and low test concentrations, respectively. Measured concentrations in flow-through test systems ranged from undetectable to a maximum of 0.10 μg/L for

Table 5. Results of chemical analyses and mortality of test animals for sediment-sorbed fenvalerate in static and flow-through test systems

	Nominal sediment concn. (mg/kg)		
	10	1.0	0.1
Static test systems			
Measured concn. over 10 d			
Sediment	10–13 mg/kg	1.2–1.6 mg/kg	0.097–0.19 mg/kg
Water	0.2–1.9 μg/L	0.06–0.17 μg/L	ND–0.03 μg/L
Water (theoretical)	0.6 μg/L	0.06 μg/L	0.006 μg/L
Mortality			
Mysids (LC50 0.008 μg/L)	100%[a]	100%[a]	58%[a]
	100%[b]	100%[b]	70%[b]
Grass shrimp (LC50 0.003 μg/L)	100%[a]	100%[a]	48%[a]
Pink shrimp (LC50 0.84 μg/L)	100%[a]	0%[a]	0%[a]
	100%[b]	0%[b]	0%[b]
Flow-through test systems			
Measured concn. over 10 d			
Sediment	8.4–10.7 mg/kg	0.95–1.8 mg/kg	0.12–0.15 mg/kg
Water	ND–0.10 μg/L	ND–0.04 μg/L	ND–0.04 μg/L
Water (theoretical)	0.6 μg/L	0.06 μg/L	0.006 μg/L
Mortality			
Mysids (LC50 0.008 μg/L)	100%[a]	30%[a]	16%[a]
	100%[b]	33%[b]	53%[b]
Grass shrimp (LC50 0.003 μg/L)	100%[a]	98%[a]	25%[a]
Pink shrimp (LC50 0.84 μg/L)	63%[a]	0%[a]	0%[a]
	80%[b]	0%[b]	0%[b]

LC50s from Table 3. ND, not detectable (<0.02 μg/L in water, <0.005 mg/kg in sediment).
[a]Mortality of test animals exposed on days 1 to 4.
[b]Mortality of test animals exposed on days 1 to 10.

the high test concentration, and to 0.04 μg/L in the medium and low test concentrations.

In static tests, nominal sediment concentrations of 0.1 mg/kg fenvalerate or greater resulted in acute lethal effects in mysids and grass shrimp, whereas pink shrimp were affected only in the system with sediment contaminated at 10 mg/kg. Mortality of mysids and grass shrimp was lower in the 0.1 and 1.0 mg/kg flow-through systems. However, exposure to sediment contaminated at 10 mg/kg resulted in 100% mortality in all three species. The mortality of pink shrimp was 63% after 96 h of exposure and 80% after 10 d of exposure in 10 mg/kg test systems under flow-through conditions.

Cypermethrin

Measured concentrations of cypermethrin in test sediment ranged from 40 to 100% of nominal concentrations (Table 6). Concentrations ranged from 0.4 to 0.6 mg/kg in the 1.0 mg/kg nominal test system, from 0.05 to 0.1 mg/kg in the 0.1 mg/kg sediment and from less than 0.005 to 0.007 mg/kg in the 0.01 mg/kg sediment. Cypermethrin was not detected in water samples collected during static and flow-through tests. Water concentrations in the static systems should have exceeded the 0.02 μg/L detection limit, calculated by sediment/water partitioning based on cypermethrin's log *P* value and the sediment organic content [14].

Under static conditions, sediment contaminated with cypermethrin at 1 mg/kg was acutely lethal to all test species; that contaminated with 0.1 mg/kg was lethal to 85% of the mysids and 28% of the grass shrimp. At 0.01 mg/kg, only 12% of the mysids died in the 4-d test and all survived the 10-d test. Sediments contaminated at 0.1 mg/kg in mysid and grass shrimp tests and at 1.0 mg/kg in pink shrimp tests were less toxic under flow-through conditions than under static conditions.

DISCUSSION

Mortality in the test populations of mysids, grass shrimp and pink shrimp clearly delineated (a) the degree of sediment contamination necessary to obtain acute, lethal effects in marine crustaceans in laboratory test systems; (b) the reduction of tox-

Table 6. Results of chemical analyses and mortality of test animals for sediment-sorbed cypermethrin in static and flow-through systems

	Nominal sediment concn. (mg/kg)		
	1.0	0.1	0.01
Static test systems			
Measured concn. over 10 d			
Sediment	0.4–0.6 mg/kg	0.06–0.08 mg/k	ND–0.006 mg/kg
Water	ND	ND	ND
Water (theoretical)	0.12 μg/L	0.012 μg/L	0.0012 μg/L
Mortality			
Mysids (LC50 0.005 μg/L)	100%[a]	85%[a]	12%[a]
	100%[b]	85%[b]	0%[b]
Grass shrimp (LC50 0.016 μg/L)	100%[a]	28%[a]	0%[a]
Pink shrimp (LC50 0.036 μg/L)	70%[a]	0%[a]	0%[a]
	73%[b]	0%[b]	0%[b]
Flow-through test systems			
Measured concn. over 10 d			
Sediment	0.4–0.6 mg/kg	0.06–0.10 mg/kg	0.005–0.007 mg/kg
Water	ND	ND	ND
Water (theoretical)	0.12 μg/L	0.012 μg/L	0.0012 μg/L
Mortality			
Mysids (LC50 0.005 μg/L)	100%[a]	5%[a]	5%[a]
	100%[b]	25%[b]	10%[b]
Grass shrimp (LC50 0.016 μg/L)	100%[a]	4%[a]	0%[a]
Pink shrimp (LC50 0.036 μg/L)	18%[a]	0%[a]	0%[a]
	23%[b]	0%[b]	0%[b]

LC50s from Table 4. ND, not detectable (<0.02 μg/L water, <0.005 mg/kg sediment).
[a]Mortality of test animals exposed on days 1 to 4.
[b]Mortality of test animals exposed on days 1 to 10.

icity under flow-through conditions; and (c) the relative sensitivities of these test species. Direct contact with or ingestion of contaminated sediment did not appear to enhance the toxicity of fenvalerate or cypermethrin to mysids, grass shrimp or pink shrimp. The role of suspended sediment and TOC in mediating animal exposures to pyrethroids was not addressed in our research, although they are recognized as factors of potential significance. Mortality could be explained by comparisons of each species' LC50 with measured or theoretical aqueous concentrations of fenvalerate and theoretical concentrations of cypermethrin in our test systems. Assessments of the bioavailability of pyrethroids in complex systems should focus on characterizations of aqueous concentrations to produce a basis for evaluating the potential for acute lethal effects.

In other tests at our laboratory, sediment-sorbed chemicals were not acutely toxic to grass shrimp or amphioxus until concentrations in sediment were increased to the point where partitioning into overlying water resulted in acutely lethal concentrations [14]. These tests were conducted in differently configured test systems and while using sediments contaminated with fenvalerate, cypermethrin, tributyltin oxide, triphenyltin oxide, trichlorobenzene or di-*n*-butyl phthalate. Similar sediment/water partitioning relationships were discussed by Muir et al. [6] and Hill [1] for pyrethroids in freshwater systems and by McLeese and Metcalf [19] for organochlorine insecticides in saltwater systems. Sorption to particulate and dissolved organic matter has been a major factor in assessing the bioavailability and toxicity of pyrethroids added to freshwater ponds [4,5,20].

Tagatz and Ivey [21] described the effects of aqueous-source fenvalerate on benthic marine communities that colonized sandy sediments. Numbers of individuals and species of arthropods (including crustaceans) were significantly reduced by an 8-week exposure to 0.1 μg/L fenvalerate in flowing seawater; numbers of species among all benthic phyla were reduced in 10 μg/L fenvalerate. Numbers of species were reduced in communities that developed in sediment contaminated with fenvalerate at 10 mg/kg followed by colonization for 8 weeks [22]. These results also show that fenvalerate was less toxic when sorbed to sediments; however, characterization of fenvalerate concentrations in pore water and in the upper layers of surface sediment would be necessary to facilitate quantitative comparisons.

Comparison of laboratory and field data

The high degree of correspondence between theoretical concentrations of fenvalerate or cypermethrin in water overlying contaminated sediment in static systems and our expectations of survival of the test species based on LC50s from aqueous exposures suggests that chemical partitioning between contaminated sediments and overlying water may be modeled to predict acute lethal effects on marine crustaceans for habitats with well-defined physicochemical and hydrodynamic characteristics. The presence of pyrethroid in sediment or water samples is not a sufficient basis for predicting toxic effects on marine biota; studies of pyrethroid insecticides in complex, natural systems must focus on chemical exposures. To validate risk assessments, a comprehensive evaluation of chemical dynamics, biotic exposure–response relationships, and field observations on biotic composition from the species, population and community perspectives are needed.

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